Support Information

Polymerization Behavior of Biscarbenes Derived by Thermolysis of Bisdiazo Compounds

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1 Synthesis and characterization

1.1 Reagents for synthesis

All the chemicals and solvents were purchased from commercial manufacturers and used as received unless stated otherwise. Here is the basic information about each one chemical reagent used in synthesis and purification.

4-Phenoxyaniline (purity >97.0%) and Celite[®] (325 mesh powder) were purchased from Alfa Aesar.

Trifluoroacetic anhydride (TFAA, purity >98.0%GC), aluminum chloride (AlCl₃, purity>98.0%), isophthaloyl chloride (purity >99.0%), glacial acetic acid (99.9985% metal basis) obtained from Tokyo Chemical Industry (TCI, Shanghai, China).

Acetone (AR, >98.5%), Potassium permanganate (KMnO₄, AR, purity > 99.5%) and Magnesium sulfate (MgSO₄, AR) were purchased from General-Reagent

dichloromethane (DCM, AR), ethanol anhydrous (EtOH, AR), sodium hydroxide (NaOH, AR). manganese sulphate tetrahydrate (MnSO₄·4H₂O, AR, purity > 98.0%), sodium sulfate (Na₂SO₄, AR), potassium hydroxide (KOH, AR) supplied by Sinopharm Chemical Reagent Co., Ltd.

Pyridine (99.5%) was from Adams-beta, and hydrazine monohydrate (37%, purity >98.0%(T)) from Aladdin. All D-Substituted solvents are provided by Cambridge Isotope Laboratories, Inc.

Active Manganese dioxide (MnO₂) was prepared freshly based on a modified method reported by Attenburow et al.¹ and the details were showed below. Briefly, an aqueous solution by dissolving 16 g of KMnO₄ in deionized (DI) water of 100 mL, stirring and being heat up to 90°C on a hotplate. Another aqueous solution of 18.5 g $MnSO_4 \cdot H_2O$ in DI water of 25 mL and 19.5 mL of 40%wt NaOH aqueous solution were added into the above prepared KMnO₄ solution in portion wise at the same time. Please be careful since too much of such addition made the stirring solution mixture split out and could hurt the exposed skin. After addition, keep stirring at that temperature for another hour. Then cool it down to room temperature naturally. Vacuum filtration to get wet cakes. Redissolved some of the wet cakes in DI water and centrifugation at 15000 rpm for 20 min and repeat such centrifugation and wash with DI water until the supernatant after centrifugation become colorless. Afterwards, the settlement was collected and dried in an oven of 120°C overnight (~16 h). Finally, the powder was collected by griding and stored sealed vial in dark isolated from air as much as possible.

Bisdiazo compounds are quite high energy compounds and should be handled with caution, and all the experiment upon heating is fulfilled in fume hood with slash hard enough for safety concerns. Hydrazine monohydrate is highly toxic and needs to be handled based on the established safety protocols.

1.2 General Characterization

Elemental analysis of each bisdiazo compound was carried out at Elementar Unicube CHNS/O Analyzer (Elementar Analysensysteme GmbH, Germany), and the averaged data obtained by duplicates for each sample.

Optical and fluorescence microscopy images of all the bisdiazo compounds were obtained by compressing their solid powder crystal/pellet onto a glass slide and then observation at the objective lens 10× with an exposure time of 1.33s by

using the Olympus BX 53 system on both green field with λ_{ex} =460-495 nm and blue field with λ_{ex} =360-370 nm in a dark room at ambient conditions.

The analysis of functional groups present was done using an attenuated total reflection (ATR) Fourier transform infrared spectroscopy (ATR-FTIR, IRAffinity-1s, Shimadzu). The spectral window for the analysis was 4000-600 cm^{-1} at a resolution of 4 cm^{-1} over 16 scans.

The ¹H and ¹³C Nuclear Magnetic Resonance (NMR, JNM-ECZ400S, JEOL, Japan) spectra were recorded at 400 MHz (varied frequencies for ¹³C due to different solvents) at room temperature.

Ultraviolet visible spectroscopy (UV-vis, UV-1900 spectrometer, Shimadzu) were used for the bisdiazo compounds and their corresponding polymerized ones in THF solution in the wavelength of 200-700 nm with a scanning speed of 10 nm/min at room temperature.

Thermogravimetric analysis (TGA) measures the amount and rate of change in sample weight as a function of temperature or time. TGA was carried out using a TGA 5500 Thermal Analyzer (TA Instrument, USA) at a heating rate of 5 °C/min under an argon atmosphere with a flow rate of 50 mL/min.

Differential scanning calorimetry (DSC) and stepwise isothermal DSC. General thermal profile was carried out by using differential scanning calorimeter (DSC Q2000, TA Instruments, USA) at heating of 5 °C/min with a nitrogen flow rate of 50 mL/min over the temperature range from 0 to 200°C. The stepwise isothermal DSC used a heating rate of 20 °C/min from 0 to 140°C and isothermal at certain temperatures (60, 80, 100, 120 and 140°C) for 30 min under nitrogen atmosphere. The sample mass ranged from 3-5 mg for general DSC testing and 5-7 mg for stepwise isothermal running. All the samples were prepared in hermetically sealed DSC tins, due to release of nitrogen during the heating up process.

1.3 Synthesis of bisdiazo compounds with varied terminal groups

1.3.1 Synthesis of compound Bisdiazo-H

The bisdiazo-H compound was synthesized in house by the procedure described in previous publications that used in polymer surface modification ²⁻⁴. Here, the characterized results of each one involved were shown in **Scheme S1** here.





Bisketone-H (aka,1,3-EKKE)

¹H-NMR (400 MHz, DCM-D₂) δ(ppm): 8.09 (t, *J* = 1.7 Hz, 1H), 7.98 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.89 – 7.76 (m, 4H), 7.69 – 7.57 (m, 1H), 7.50 – 7.35 (m, 4H), 7.22 (ddt, *J* = 8.7, 7.4, 1.1 Hz, 2H), 7.16 – 6.96 (m, 8H).

 $^{13}\text{C-NMR}$ (101 MHz, DCM-D_2) $\delta(\text{ppm})$: 194.70, 162.35, 155.87, 138.55, 133.32, 132.80, 131.87, 131.09, 130.51, 128.88, 125.11, 120.62, 117.57.

1-((E)-Hydrazineylidene(4-phenoxyphenyl) methyl)-3-((Z)-hydrazinylidene(4 phenoxyphenyl)methyl)benzene



The mixture after refluxing was cooled to room temperature naturally, water (50 mL) was added, giving a suspension. The mixture was filtered, and the precipitate was dried in an oven. The crude product (~77%) of a light-yellow solid as a mixture of diastereoisomers was used without further purification.

¹H-NMR (500.3 MHz, DMSO-d6) δ(ppm): 6.16–6.54 (m, 4H), 6.90–7.56 (m, 22H).

 13 C-NMR (125.8 MHz, DMSO-d6) $\delta(ppm):$ 118.7, 118.8, 119.1, 119.5, 119.6, 119.7, 123.3, 123.9, 124.3, 124.4, 125.0, 125.9, 126.2, 127.5, 127.6, 127.8, 127.9, 128.3, 129.6, 129.8, 130.5, 130.6, 130.8, 131.1, 131.2, 133.3, 134.7, 134.8, 135.0, 139.3, 140.6, 143.3,143.4, 144.2, 144.4, 156.5, 156.7, 157.0, 157.2, 157.4.

IR *u_{max}* (cm⁻¹): 3403, 3039, 2922, 1586, 1502, 1486, 1232, 1164, 1070.

1,3-Bis(diazo(4-phenoxyphenyl)methyl)benzene



The mixture was vigorously stirred for 2 hr in the dark and then filtered through a pad of Celite[™]. The filtrate was concentrated under vacuum to yield crude products labeled as Bisdiazo-H (~90%) as a purple solid and then stored at sub-ambient temperature (4°C) in dark to avoid decomposition.

¹H-NMR (400 MHz, DCM-D₂) δ(ppm): 7.88 – 5.98 (m, 22H).

¹³C-NMR (101 MHz, DCM-D₂) δ(ppm): 159.67, 157.51, 156.74, 156.12, 133.48 – 132.55, 131.75, 130.99 – 129.91, 129.22, 128.37, 128.18 – 127.27, 126.31, 126.12 – 125.43, 124.96, 124.67 – 123.52, 121.83, 120.61, 120.30 – 119.63, 119.33, 118.37 – 117.27, 62.28, 54.31.

IR *v_{max}* (cm⁻¹): 3039, 2031, 1588, 1503, 1486, 1234, 1165.

1.3.2 Synthesis of compound Bisdiazo-Me



Scheme S2. Simplified procedure of synthesizing bisdiazo-R compound (R=Me and NO₂).

The modified synthesis procedure of both bisdiazo-Me and bisdiazo-NO₂ are almost the same with different starting materials as shown in **Scheme S2**, which are 1-methyl-4-phenoxybenzene and 1-nitro-4-phenoxybenzene, respectively.

1,3-Phenylenebis((4-(p-tolyloxy)phenyl)methanone)



To a flask (100 mL) of 40 mL DCM, AlCl₃ (950 mg, 7.1 mmol, 2.5 eq) was added to the above mixture while that mixture being stirred vigorously (vortex starting) in the ice/water bath of 0^{5} °C, and followed by adding isophthaloyl chloride (290 mg, 1.42 mmol, 0.5 eq) and 1-methyl-4-phenoxybenzene (2.84 mmol, 1.0 eq) in sequence, and such mixture being stirred in an ice/water bath, and such mixture was continue stirred at room temperature (r.t) for another 2 hr. After the reaction is done, the mixture was poured into pre-cooled DI H₂O (40 mL) and stirred vigorously for at least 30 min at r.t, followed being transferred into a separation funnel. Afterwards, the aqueous phase was extracted with DCM (30 mL×4) and the combined organic phase was wash with DI H₂O (100 mL×4) and brine (50 mL×5), then dried over anhydrous Na₂SO₄ and the filtrate was collected and purified through flash column silica eluent with hexane/DCM (DCM% from 20 to 100%), solvent was removed by the rotary evaporator, and finally the pale-yellow solid was collected to yield a bisketone-Me sample termed 1,3-phenylenebis((4-(*p*-tolyloxy)phenyl)methanone) (455 mg, ~ 33 %).

¹H-NMR (400 MHz, DMSO-*D*₆) δ(ppm): 7.96 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.89 (t, *J* = 1.7 Hz, 1H), 7.83 – 7.75 (m, 4H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.17 (m, 4H), 7.06 – 6.97 (m, 8H), 2.29 (s, 6H).

¹³C-NMR (101 MHz, DMSO-*D*₆) δ(ppm): 193.67, 161.76, 152.42, 137.42, 134.18, 132.88, 132.47, 130.71, 130.21, 129.10, 120.19, 116.70, 20.34.

1-((E)-Hydrazineylidene(4-(p-tolyloxy)phenyl)methyl)-3-((Z)-hydrazinylidene(4-(p-tolyloxy)phenyl)methyl)benzene

After the work-up, the solvent DCM was removed via rotary evaporator. This yielded a light-yellowed solid which was a mixture of diastereomers and was used without further purification (179 mg, \sim 65 %).

¹H-NMR δ(ppm): 6.65-7.50 (aromatic H), 3.92-4.06 (amine 4H), 2.20-2.35 (methyl 2H)

¹³C-NMR δ(ppm): 20.85, 158.06, 157.86, 157.12, 154.61, 154.57, 154.18, 154.05, 144.58, 144.33, 143.36,140.65, 139.38, 134.36, 133.75, 133.66, 133.37, 133.22, 131.20, 131.09, 131.06, 130.93, 130.25, 130.20, 129.81, 128.33, 127.93, 127.88, 127.55, 120.03, 119.89, 119.41, 119.22, 118.97, 118.94, 118.83, 118.27.

IR(cm⁻¹): 2959,2926, 2855, 1599 (C=N), 1590, 1496, 1235.

1,3-Bis(diazo(4-(p-tolyloxy)phenyl)methyl)benzene



After the reaction is done, the mixture was then filtered through Celite[®], the filtrate was evaporated in vacuo to yield a Bisdiazo-Me, and such final product was stored in a fridge (4°C) for future use (221 mg, 97 %). ¹H-NMR(400 MHz, DMSO- D_6) δ (ppm): 7.55 – 6.55 (m, 20H), 2.31 – 2.16 (m, 6H).

¹³C-NMR(101 MHz, DMSO-*D*₆) δ(ppm): 154.44, 133.49, 130.98, 130.48, 128.15, 121.52, 119.49, 118.59, 61.84, 20.80. IR(cm⁻¹): 2959,2926, 2855, 2032 (N=N), 1590, 1497, 1230, 1161

1.3.3 Synthesis of compound Bisdiazo-NO₂

Bisdiazo-NO₂ is almost the same synthesis procedure as shown in **Scheme 2**, but with different starting materials, 1-nitro-4phenoxybenzene, afford an off-white solid with yield (455 mg, ~ 33 %) after being purified through flash column eluting with hexane/DCM (DCM from 22% to 100%). If there is some kind of gel like sample of bisketone-NO₂ after being in vacuo, it might be some lower molecular weight impurities that could be removed by discoloration with 1.5% weigh/volume active carbon boiling in DCM for at least 30 min. Then, followed by a reduction with hydrazine under AcOH catalization and being oxidated for the purplecolored Bisdiazo-NO₂ compound.

1,3-Phenylenebis((4-(4-nitrophenoxy)phenyl)methanone)



Similar synthesis procedure as that for bisdiazo-Me, just using alternative starting compound, 1-nitro-4-phenoxybenzene. ¹H-NMR(400 MHz, DCM-D₂) δ (ppm): 8.31 – 8.21 (m, 4H), 8.18 (td, *J* = 1.8, 0.6 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.97 – 7.83 (m, 4H), 7.75 – 7.63 (m, 1H), 7.30 – 7.08 (m, 8H).

¹³C-NMR(101 MHz, DCM-D₂) δ(ppm): 194.57, 162.14, 159.54, 144.08, 138.27, 133.98, 133.71, 133.01, 131.20, 129.08, 126.44, 119.84, 118.99.

IR(cm⁻¹): 3093, 1654 (C=O), 1577, 1508, 1338 (N=O), 1226, 1161, 1103

1-((E)-hydrazineylidene(4-(4-nitrophenoxy)phenyl)methyl)-3-((Z)-hydrazinylidene(4-(4-nitrophenoxy)phenyl)methyl)benzene



¹H-NMR δ(ppm): 8.14-8.27 (aromatic 4H next to NO₂), 7.86-6.99 (aromatic H), 5.51 (amine H, 4H) ¹³C-NMR δ(ppm): 117.3, 117.85, 120.1, 121.2, 124.2, 125.8, 126.3, 126.9, 128.0, 128.3, 129.4, 129.7, 130.7, 131.1, 132.8, 134.1, 135.8, 138.5, 140.0, 142.7, 143.3, 146.4, 147.3, 154.5, 155.6, 162.6, 163.1 IR(cm⁻¹): 3417, 3294, 3070, 1581, 1481, 1342 (N=O), 1234, 1157, 1103, 1010

1,3-Bis(diazo(4-(4-nitrophenoxy)phenyl)methyl)benzene



¹H-NMR (400 MHz, DMSO-*D*₆) δ(ppm): 8.39 – 8.10 (m, 4H), 7.80 – 6.91 (m, 16H), 6.50 (d, *J* = 38.1 Hz, 1H). ¹³C-NMR (101 MHz, DMSO-*D*₆) δ(ppm): 163.30, 153.09, 142.92, 130.65, 128.22 – 127.59, 126.75, 122.14, 120.81, 118.04, IR(cm⁻¹): 3394, 3086, 2036 (N=N), 1581, 1489, 1335 (N=O), 1242, 1157, 1110

1.3.4 Synthesis of compound Bisdiazo-NH₂

Here, the resulting bisdiazo compound labeled as bisdiazo-NH₂ was similar to that of bisdiazo-H compound and **Scheme S3** briefly describes the synthesis procedure.



Scheme S3. Simplified procedure of synthesizing bisdiazo-NH₂ compound.

2,2,2-Trifluoro-N-(4-phenoxyphenyl)acetamide



The reaction was then stirred at r.t. for overnight. Remove the solvent by rotary evaporator, 10 mL of acetone was added and then the mixture was poured into cold DI water (100 mL, pre-cooled in 4°C fridge) and stirred for 10 min, filtration via general filer paper, the solid was dried at 80°C in oven for overnight (~84%).

ATR-IR(cm⁻¹): 3290 (N-H),1701 (C=O), 1172 (C-F), 1149 (C-F),

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.99-7.05(m, 4H), 7.13(t, 1H), 7.33-7.38 (m, 2H), 7.50-7.54(m, 2H).

¹³C-NMR(101 MHz, CDCl₃) δ(ppm): 114.4, 117.3, 119.1, 119.5, 122.4, 123.8, 130.0, 130.2, 154.7, 155.0, 155.6, 158.9.

HRMS (ESI-): observed *m/z* 281.07376, C₁₄H₁₀F₃NO₂- requires *m/z* 281.07364

N,N'-(((Isophthaloylbis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))bis(2,2,2-trifluoroacetamide)



The mixture continued stirred at r.t. for another 2 hr. The reaction solvent was removed via rotary evaporator. 10 mL acetone was added, and then poured into cold DI water (200 mL pre-cool in 4°C fridge). After filtration via general filter paper, the solid was

dried in oven at 80°C overnight. the solid was redispersed in DCM (enough to dissolve the chemical residues, the product is still solid) and the solid was filtered via filter paper and dried in fume hood at RT to yield white solid (~ 68%).

ATR-IR(cm⁻¹): 3278(N-H), 1705(C=O, amide), 1651(C=O, ketone), 1178(C-F), 1150(C-F).

¹H NMR (400 MHz, DMSO-*D*₆) δ(ppm): 11.34 (s, 1H), 8.09 – 7.91 (m, 2H), 7.89 – 7.66 (m, 5H), 7.33 – 6.98 (m, 4H).

¹³C NMR(101 MHz, DMSO-*D*₆) δ(ppm): 193.71, 161.29, 154.62, 154.26, 152.03, 137.43, 133.02, 132.53, 131.08, 130.15, 129.07, 123.02, 120.73, 120.12, 117.16, 114.38.

¹⁹F NMR (376 MHz, DMSO- D_6) δ (ppm): -73.76, -73.81 (d, *J* = 12.7 Hz).

HRMS (ESI+): observed m/z 693.1450, $C_{36}H_{23}F_6N_2O_6$ + requires m/z 693.1454.

4,4'-((((1Z,1'Z)-1,3-Phenylenebis(hydrazineylidenemethylene))bis(4,1-phenylene))bis(oxy))dianiline



The mixture after refluxing for 40 hr was cooled to r.t. naturally and the solvent was evaporated in vacuo. DCM (50 mL) was added to the remaining residue, and then washed with DI water (4×50 mL). The organic layer (lower one, since DCM is heavier in density than water) was then dried over MgSO₄, filtration and the organic phase was evaporated in vacuo. This yielded a yellow solid was a mixture of diastereomers and used without further purification (~70 %).

IR (neat, cm⁻¹): 3350 (N-H, amine), 3426 (N-H, hydrazone), 3040 (C-H, aromatic), 1601 (C=N).

¹H-NMR (400 MHz, CDCl₃) δ(ppm): 3.52 (s, 4H), 5.12-5.64(m, 4H), 6.63-6.74(m, 5H, aromatic), 6.84-6.93(m, 7H, aromatic), 6.98-7.05(m, 1H, aromatic), 7.09-7.22(m, 3H, aromatic), 7.30-7.62 (m, 4H, aromatic).

HRMS (ESI+): observed m/z 529.23462, $C_{32}H_{29}N_6O_2$ + requires m/z 529.23465.

4,4'-(((1,3-Phenylenebis(diazomethylene))bis(4,1-phenylene))bis(oxy))dianiline



The reaction mixture was then filtered through Celite[®]. The filtrate was evaporated in vacuo to yield a dark red solid, which is the final product was stored in a fridge of 4°C in dark for future use (~ 97 %).

ATR-IR(cm⁻¹): 3437, 3344, 3039(C-H, aromatic), 2022 (N=N), 1593, 1496, 1222.

 1 H NMR (400 MHz, DCM-D₂) δ (ppm): 7.51 – 6.73 (m, 4H), 6.72 – 6.58 (m, 1H), 3.66 (s, 1H).

¹³C NMR (101 MHz, DCM-D₂) δ(ppm): 158.01, 148.44, 147.83, 143.97, 131.79, 130.46, 130.02, 129.07, 127.79, 125.76, 122.51, 122.35 – 121.63, 121.43, 120.21, 118.33, 117.47, 116.63, 116.34, 114.93, 62.13, 54.31.

HRMS (ESI+): observed m/z 525.2035, $C_{32}H_{25}N_6O_2$ + requires m/z 525.2033.

- 1.4 Nuclear Magnetic Resonance (NMR) spectrum of bisketone and bisdiazo compounds
- (1) Bisketone-H in DCM-D2: proton and ¹³C





(2) Bisdiazo-H (alternative name is 1,3-EKKE) in DCM-D2: proton and ¹³C

(3) Bisketone-Me in DMSO-D6: proton and ¹³C



(4) Bisdiazo-Me in DMSO-D6: proton and ¹³C



(5) Bisketone-NO₂ in DMSO-D6: proton and ¹³C



(6) Bisdiazo-NO₂ in DCM-D2: proton and ^{13}C



(7) Bisketone-NHCOCF₃ in DMSO-D6: proton, ¹³C and ¹⁹F



13









2 Thermal treatments experiments

2.1 Thermal stability via thermogravimetric analysis (TGA)

Thermal properties of bisdiazo compounds with varied terminal groups were investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) that are summarized in Figure S1a-S1d. Figure S1 and S1b for the TGA and derivative thermogravimetry (DTG) traces, respectively. On the other hand, Figure S1c-S1d sketched the DSC traces of all the bisdiazo compounds, which exhibits a major broad exothermal peak at higher temperature and a tiny glass transition band at lower temperature. Since the major exothermal peak is quite broad and a stepwise isothermal DSC method was introduced for trying to figure out and/or serveral sub-broad peak(s) at certain temperature within such a broad exothermal range, the expected of which are illustrated in Figure 2 in main text. Figure S1e illustrated the accumulated weight loss of both bisdiazo compounds from its thermogravimetric analysis (TGA) curves as shown in Figure S1a, and such accumulated weight loss exhibits a certain trend with temperature increases, which is approaching the approximated 10% in molecular lever but wasn't even at higher temperature of 180 °C. Figure S1g and Figure 2a-2c portrayed the stepwise isothermal DSC traces at various temperatures of bisdiazo-H, bisdiazo-Me, bisdiazo-NO₂, and bisdiazo-NH₂, respectively.





Figure S1. Thermal properties of bisdiazo-R compounds: (a) TGA and (b) DTG curves, DSC traces of (c) bisdiazo-H and bisdiazo-NH₂ and (d)bisdiazo-Me and bisdiazo-NO₂. (e) Accumulated weight loss rate (wt%) at certain temperatures from TGA curves and (f) theoretical estimated molecular weight loss by releasing nitrogen for bisdiazo-H and bisdiazo-NH₂. Stepwise isothermal DSC traces at various temperatures of (g) bisdiazo-Me.

2.2 Thermal analysis of bisdiazo compounds in solid phase in open-air

About 30 mg of each bisdiazo compound, bisdiazo-H and bisdiazo-NH₂, in transparent glass vial in an oil-bath of 90°C heating for 3 hr. The vial is kept open all the time till nothing changes to the bisdiazo compounds that could be perceived by naked eyes. Images as shown in Figure S2a-S2b were taken at certain times as noted in the upper left of each image. The images for bisdiazo-H were taken carefully while bisdiazo-NH₂ were in quite long-time interval until insignificant changes occur. All the observations in Figure S2a-S2b combined with the results in Figure 3 in main text implies that the polymerization of bisdiazo compounds could be carried out at a condition of oxygen tolerance one, but due to the energetic nature of bisdiazo compounds for storage such polymerization should be carried out at very low amount scale in a significantly open-space, so that there is no explosion going to happen that put all the surroundings in danger. Again, such polymerization in an open container is also under consideration for safety, which is of great help on releasing the free nitrogen in a timely manner without any further accumulation in a limited space or container.

The temperature of 90°C was chosen for such preliminary experiment is based the temperature peak in derivative thermogravimetry (DTG) curves as showed in Figure S1b that the TGA test was carried out in the same fashion of in an open sample pan while being heated up. The molecular weight under varied conditions is summarized in Table S1, and the detailed comparison among the GPC traces is presented in Figure S3a and ATR-FTIR demonstrated in Figure S3b.



Figure S2. Observation of bisdiazo- NH_2 solid being heated at 90 °C for 3 hr in air: (a) bisdiazo-H and (b) bisdiazo- NH_2 , (c) solubility evaluation of bisdiazo- NH_2 based polymer in organic solvents after solid-phase heating in open-air.





Figure S3. (a) GPC traces in THF solution and (b) ATR-FTIR spectrum of bidiazo-H after self-polymerization in solid-phase at varied conditions (in open-air and nitrogen atmosphere).

2.3 UV-Vis kinetic study of catalyst-free polymerization in liquid-phase

2.3.1 Kinetic study in varied solvents at different temperatures

Figure S4 illustrated UV-Vis kinetic traces observed about the catalyst-free polymerization of bisdiazo-H, bisdiazo-Me and bisdiazo-NO₂ at higher temperatures in solvents of toluene at 100°C and chlorobenzene at 120°C, respectively. There is a noticeable shoulder band in UV-Vis traces for the polymerization of bisdiazo-H and bisdiazo-Me in both solvent-temperature combinations as highlighted with black-dash boxed in Figure S4a-S4d, which is not observed for bisdiazo-NO₂ at either temperature (Figure S4e-S4f). Besides, the intensity of major UV-Vis band at about 295 nm would be lowered as polymerization continues and then increased after polymerization for 18 hr and longer for both bisdiazo-Me and bisdiazo-NO₂ at higher temperatures, especially for bisdiazo-NO₂ at temperature of 120°C since the intensity of UV-Vis band at 295 nm would be increased after polymerization for at least 2 hr (inset chart in Figure S4e-S4f). This observation is less likely to happen for bisdiazo-H polymerized in either toluene or chlorobenzene (Figure S4a-S4b), which is later explained by the following two-step consecutive polymerization carried out at higher temperatures described by both Eq.(S10) and Eq.(S11).



Figure S4. UV-Vis kinetic patterns of bisdiazo-H (a, d, g), bisdiazo-Me (b, e, h) and bisdiazo-NO₂ (c, f, i) compounds in solvents of THF @ $66^{\circ}C$ (a, b, c), toluene @ $100^{\circ}C$ (d, e, f) and chlorobenzene @ $120^{\circ}C$ (g, h, i).

(1) Simplified kinetic reaction analysis

Determination of reaction rate of constants and conversion would be of great help on understanding how the consumption rate of the bisdiazo compounds with varied terminal groups and possible for the polymerization progress. And hereby it was based on the intensity of UV-Vis major feature band absorption at 290 nm for all the polymerization reactions, which are illustrated by a simplified equation as shown below in Eq. (S1). In Eq. (S1), A_0 stands for the initial concentration bisdiazo compound before reaction starts, and the only reaction occurs at the diazo sites that release nitrogen upon heating, leading to a varied UV absorption A_t that is decreasing along with reaction/polymerization time.

$$Conversion(\%) = \frac{A_0 - A_t}{A_0} * 100 \ (\%) = \left(1 - \frac{A_t}{A_0}\right) * 100 \ (\%)$$
Eq. (S1)

As can be implied from the fitted lines of the collects A_t/A_0 of bisdiazo-R compounds in both THF at 66°C and toluene at 100°C as demonstrated in Figure S5a and S5c, the consumption rate of bisdiazo compounds upon heating only is kind of dependency on the terminal groups and solvent-temperature effect as well. As to the terminal group dependency, it takes less than 3 hr for both R=H and R=Me and would be doubled up to 10 hr for both R=NO₂ and NH₂ to reach its own reaction plateau (Figure S5a). As to the solvent-temperature effect, the time for consuming bisdiazo-R compounds would be noticeable around 4 hr to reach reaction plateau (Figure S5c), which is also very clearly supported by the comparison between solvent-temperature effect on the polymerization of bisdiazo-NH₂ as portrayed in Figure S5e.

As from the fitted lines showed in Figure S5a and S5c, it could be further rewriting the simplified conversion calculation as the following Eq. (S2), which could be explored a parameter, the observed reaction rate of constants (K_{obs}), that almost describes the linear portion of those fitted lines as showed in Figure S5b and S5d.

$$Conversion(\%) = 1 - exp(-k_{obs} \cdot t) - \frac{C_0}{A_0}$$
Eq. (52)

where, C_0 is the fitted/empirical constant.

As can be told from Figure S5a, the observed reaction rate of constants (K_{obs}) from the linear part as can be implied from the equation from higher to lower is that of bisdiazo-NO₂ tops, followed by bisdiazo-Me, which are significantly higher than bisdiazo-H and bisdiazo-NH₂, the latter of which is the lowest via polymerization in THF at temperature of 66°C. On the other hand, the overall conversion (%) of polymerization lasts for up to 24hr is in the order of bisdiazo-H, followed by bisdiazo-NO₂ that is slightly higher than that of bisdiazo-Me, and that of bisdiazo-NH₂ is lowest. In addition, both of observed reaction rate of constants (K_{obs}) and conversion rate of bisdiazo-NH₂ would be increased sharply as the polymerization temperature lifted up to 100 °C carried in toluene as showed in Figure S5e, as compared to the polymerization carried out in THF at 66°C, which might be due to the solvents effect in homogeneous chemical reactions⁵, since one possible reason might be the less polarity of toluene (0.099) than that of toluene (0.207)⁶ in such catalyst-free polymerization.





Figure S5. UV-Vis kinetic analysis on simplified reaction rates of constants (a, c, e) and conversion (b, d, f,) in solvent of THF at 66 °C (a, b) and toluene at 100 °C (c, d), and comparison (e, f) of bisdiazo-NH₂ in solvent THF and toluene.

(2) Consecutive reaction/polymerization kinetic analysis

As to the consecutive reaction/polymerization, the simplest complex reaction consists of two consecutive, irreversible elementary steps as illustrated in Figure S6a, and the following initial conditions hold immediately.

At time *t*=0, concentration of *A*, $[A]_t = [A]_0$, concentration of intermediate of *B*, $[B]_t = [B]_0$, concentration of product *C*, $[C]_t = 0$, and with at all times, $[A]_t + [B]_t + [C]_t = [A]_0$.

Then, using those equations mentioned above, the rate equation for the process and solve to determine the concentrations as function of time could be set up and as the followings:

$$\frac{d[A]_t}{dt} = -k_1[A]_t \qquad \text{Eq.(S3)}$$

$$\frac{d[B]_t}{dt} = -k_1[A]_t - k_2[B]_t \qquad \text{Eq.(S4)}$$

$$\frac{d[C]_t}{dt} = -k_2[B]_t \qquad \text{Eq.(S5)}$$

after integrating Eq.(S3) and gives

$$[A]_{t} = [A]_{0} exp^{[i0]}(-k_{1}t)$$
 Eq.(S6)

Followed by substituting Eq.(S6) into Eq.(S4) and get

$$\frac{d[B]_t}{dt} - k_2[B]_t = -k_1[A]_0 exp^{[m]}(-k_1t)$$
Eq.(S7)

as such,

$$[B]_{t} = \frac{k_{1}}{k_{2} - k_{1}} \{ \exp(-k_{1}t) - exp^{[m]}(-k_{2}t) \} [A]_{0}$$
 Eq.(S8)

Finally, $[C]_t = [A]_0 - [A]_t - [B]_t$

$$[C]_{t} = \left\{ 1 + \frac{k_{1} \exp(-k_{2}t) - k_{2} \exp(-k_{1}t)}{k_{2} - k_{1}} \right\} [A]_{0}$$
 Eq.(S9)

As comes to two special cases for a pair of sequential reactions:

- Case I with k₁>>k₂ that is suggesting all the A initial present is rapidly converted into B and then slowly used up to form C, thus reaches
 - $[C]_t = \{1 \exp(-k_2 t)\}[A]_0$

The rate of producing is becoming independent of k_1 and the second step is the rate determining step.

• Case II with $k_1 << k_2$ that is suggesting *B* is consumed as soon as it is produced since k_1 is negligible in comparison with k_2 , then the overall rate id depends only on k_1 and the first step is rate determining. Thus,

 $[C]_t = \{1 - \exp(-k_1 t)\}[A]_0$

Let's see the possible detailed polymerization of bisdiazo compounds upon heating to produce carbene species, which are highly active and energetic ones. But it has to be noted that carbene species are kind of (*i*) biscarbene and (*ii*) diazo-carbene formed through releasing one or two nitrogen upon heating from bisdiazo compounds as portrayed in Figure S6b.

$$y = y_0 + A_1 exp^{[m]} \left[-\frac{(x - x_0)}{t_1} \right] + A_2 exp \left[-\frac{(x - x_0)}{t_2} \right] = Eq.(S10)$$

The fitted lines by Eq.(S8) via Origin software (Origin Pro 2017) was explored for the UV-Vis kinetic consecutive studies of catalystfree bisdiazo polymerization upon heating in varied solvents at different temperatures, which are shown in Figure S6c-S6d with the fitted parameter for calculating the rate of constants k_1 and k_2 for each compound from such fitting are list in Table S2. Then, as can be derived from Table S2, the rate of constants for polymerization carried out in THF at 66°C, for R=H and R=NH₂ exhibits $k_1=k_2$, but for R=Me and R=NO₂ that showed $k_1 >> k_2$. While the polymerization carried out in toluene at 100°C, it would be the case of $k_1 = k_2$ for both R=H and R=NO₂ compounds polymerization.

Since the case on UV-Vis kinetic analysis of polymerization carried out in chlorobenzene at a higher temperature of 120°C, the twostep consecutive analysis was become a bit of complicated as demonstrated in Figure S6e that both R=H and R=Me still fit for the one as described by Eq.(S10), but the latter two of both R=NO₂ and R=NH₂ is not fitting any more, which was turned out to be more suitable one by the description in Eq. (S11) as showed bellowed and it also worked for both R=H and R=Me. This could be further decomposed into two portions of exponential and linear ones as exhibited in Eq. (S12) for a more suitable comparison as demonstrated in Figure S6g using the fitted parameters list in Table S3.

$$y = p_1 \exp\left(\frac{-x}{p_2}\right) + p_3 + p_4 x$$

Eq.(11)
$$y_1 = p_1 \exp\left(\frac{-x}{p_2}\right) and \ y_2 = p_3 + p_4 x$$

Eq.(12)

The fitted kinetic contributions from both decomposed exponential y_1 and linear part y_2 for polymerization in chlorobenzene at 120°C described by both Eq.(S11) and Eq.(S12) is showed in Figure 5d for all the bisdiazo compounds, while those of bisdiazo-NH₂ in three combinations of solvent-temperature is sketched in Figure 5e-5f.

Polymerization	Constants*	R=H	R=Me	R=NO ₂	R=NH ₂
THE/66°C	t ₁	2.83431	0.02967	0.03206	2.76023
	<i>t</i> ₂	2.83444	3.52481	1.5455	2.76024
Toluene/100°C	t ₁	0.31647	0.11565	2.18416	0.64539
	<i>t</i> ₂	3066830.81	6.41661	2.18411	0.64536
	p 1	5.26638	2.21872	0.75187	5.57463
Chlorobenzene/120°C	p ₂	0.66579	1.03312	1.35369	1.1402
	<i>p</i> ₃	-0.50351	-0.51098	-0.27281	-1.6458
	p_4	0.01305	0.01813	0.02402	0.16084

Table S2. Fitted parameters of a two-step consecutive polymerization

Note*: the fitted parameters (t_1, t_2) from Eq.(S10), and the fitted parameters (p_1, p_2, p_3 and p_4) are from Eq.(S11).

Lastly, making further comparison between Eq.(S9) and Eq. (S10) with the fitted t values as listed in Table S2, then the k_1 and k_2 values for all the bisdiazo compounds polymerized in both THF at 66°C and toluene at 100°C could be obtained as summed up in Table S3 in the main text. Similarly, another further comparison between Eq.(S9) and Eq. (S11) with the fitted p values as listed in Table S2, the specific k_1 and k_2 values for all the bisdiazo compounds polymerized in chlorobenezene at 120°C could be obtained as listed in Table S3. As can be implied from Table S3, one thing maybe outstanding is that the k_2 of R=Me in PhMe at 100°C is so tiny that the polymerization could be impossible to happen, but the MW traces proved it did happen and in a nice

way (Figure 5 and Table 1 in main text), and this contradicting observation may implied something could be related to the possibility of solvation effect⁷⁻¹⁰ playing quite a role in the polymerization kinetics, for instance, as similarly in the thermal decomposition of the well-known radical initiator (e.g., AIBN for 2,2'-azoisobutyronitrile) exhibiting a partial initiation rate of the solvated forms^{7, 11} for polymerization, depending on dependent on the mixture composition^{8, 9, 11}. However, for the biscarbene production and further polymerization in varied combinations of solvent-temperature, the carbene species are both the initiator-like type and monomer at the same time, which could be taken into consideration in the kinetic studies with finer experimental design and advances technique in the future. Overall and most importantly, the two-step consecutive polymerization kinetic can describe the catalyst-free polymerization kinetics of biscarbenes from thermally decomposed bisdiazo compounds in varied solvents/temperatures, though not covering all the possible angles at that time being.

			k*	R=H	R=Me	R=NO ₂	R=NH ₂	'
	/	cc°c	<i>k</i> 1	0.35	33.7	31.2	0.36	
	IHF/	66 C	<i>k</i> ₂	0.35	0.29	0.65	0.36	
	DhM	o./100°C	<i>k</i> 1	3.16	8.65	0.46	1.55	
	Phivie	e/100 C	<i>k</i> ₂	0.00004	0.16	0.46	1.55	
	PhCL	/120°C	k1	1.50	0.97	0.74	0.88	
	FIICI	120 C	<i>k</i> ₂	1.66	1.26	1.16	1.24	
(a)	A	<i>k</i> 1		→ B		<i>k</i> ₂	→ c	
(b) PhOPh R	N ₂ Ph(OPh N ₂	P	PhOPh R Biscarb	ene-R	 h	Highly active c (1) carbene C: (2) diazo C=N=	arbene C: react w/ forming C=C N forming C=N-N=C
				DiazaoCarl	oene-R			
(C) 0.0 -0.1 (0Y)YP)UI -0.3 -0.4 -0.5 -0.000 -0.041 (0Y)YP)UI -0.3 -0.4 -0.5 -0.000 -0.041 -0.56 -0.70			- Bisdiaz	zo-H/120°C zo-Me/120°C NO ₂ /120°C NH ₂ /120°C	1) 0.0 -0.1 -0.2 -0.2 -0.3 -0.4 -0.5 -0.6 -0.6		■ Bisdiazo-H/TH ● Bisdiazo-Me/T ● Bisdiazo-N0_r ● Bisdiazo-NH ₂ /T	F/66°C HF/66°C HF/66°C
-0.84	250 50	00 750 100 Time, t (min)	. 00 1250	1500 1750	-0.7	5 4.0 4.5	5.0 5.5 6.0 (In(t/min)	6.5 7.0 7.5

Table S3. The rate constants, k, for two-step consecutive polymerization of bisdiazo-R **1a-d** compounds under varied conditions.



Figure S6. (a) Scheme of consecutive reaction and/or (b) a two-step polymerization of bisdiazo-R compounds without catalyst upon heating, kinetic observations of polymerization in (c) chlorobenzene at 120°C not suitable for description by Eq.(S10), alternative kinetic observation of bisdiazo polymerized in (d) THF at 66°C and (e) toluene at 100°C described by Eq.(S11-S12), (f) plot of Hammett substituent constants, σ_{para} , and the rate constants for the combinations of temperature-solvent. (here, σ_{para} values are from reference¹²)

2.3.2 UV-Vis analysis of polymer samples in THF solution

The UV-Vis traces of final obtained polymer samples under varied solvent-temperature polymerization conditions are shown in Figure S7-S8, and the polymer could be classified as three types from the featured UV-Vis band and regardless of polymerization conditions (i.e., solvent-temperature combinations), one is for polymer from bisdiazo-NO₂ with a sharp UV peak at about 250 nm and quite small shoulder around 350 nm, one for polymer from bisdiazo-NH₂ with a quite noticeable broad UV peak at about 295 nm and the rest are for those from both bisdiazo-H and bisdiazo-Me with a small broad UV band at 285 nm and mini should around 350 nm (chemically, the latter two compounds could be regarded as one type, except more special or steric effect comes from methyl terminal group).

During the kinetic studies, we noticed that the color fading phenomenon of bisdiazo-Me in DMSO-D6 as solvent at varied temperatures was illustrated in Figure S9a is in the similar fashion as that of all bisdiazo compounds in other three organic solvents at varied temperatures, and the rate of such color fading is increase as at higher temperatures, which is also further backed up by the temperature dependence of the reaction rate and conversion as portrayed in Figure S5. Additionally, one more interesting observation is that the solvent, not just the DMSO-D6 as demonstrated in Figure S9b, including THF, toluene and chlorobenzene, are recoverable, and could reach a recover rate of at least approximately 95% in volume. From this point of view, such polymerization process is kind of recoverable as to be green chemistry type, besides no noble metal catalyst like Pd and its similar ones is needed at all. Besides, it should also be noted that the intensity at UV-Vis major band around 295 nm would decrease as time proceeds 2 hr and then increase as reaction longer to be 24 hr in DMSO-D6 at 120°C as demonstrated in Figure S9c-S9d, and this is also similar pattern as observed from Figure S4g-S4i.





Figure S7. Solvent-Temperature combination effect on Poly(Bisdiazo-R) reaction via UV-Vis measurements: (a) R=H, (b) R=Me, (c) R=NO₂ and (d) R=NH₂ (inset images are the polymer solutions in THF).



Figure S8. UV-Vis analysis of catalyst-free obtained polymer sample under varied conditions: (a)THF/66°C, (b)Toluene/100°C and (c) Chlorobenzene/120°C(UV-Vis spectrum obtained in THF solution).



Figure S9. Images of (a) color fading along the kinetic observation on catalyst-free bisdiazo-Me self-polymerization in HPLC-grade DMSO-D6 at different temperatures, (b) solvent DMSO-D6 recoverable, (c, d) UV-Vis kinetic observations on self-polymerization of bisdiazo-Me in DMSO-D6 at 120°C for 24hr.

2.3.3 UV-Vis kinetic of Pd-mediated bisdiazo polymerization upon heating

2 mol % of Pd catalyst, Bis(dibenzylideneacetone) palladium (Pd(DBA)₂, Pd content of 16.5 to 20.5%, TCl,), was explored as to that of bisdiazo compounds in HPLC-grade toluene as solvent for up to 24 hr. The UV-Vis spectrum pattern comparison of polymer between with (w/) and without (w/o) catalyst in toluene for bisdiazo compounds is summarized in Table S4.



Table S4. UV-Vis spectrum pattern comparison of polymer between with (w/) and without (w/o) catalyst in toluene as solvent.



2.4. Self-polymerization monitored by FD MS

Datamining the possible chemical formula from molecular ion under field desorption mode (FD) by using JMS-T2000GC 'AccuTOF[™] GC Alpha' system (JEOL, Japan), which is a high-resolution time of flight (HR-TOF) mass spectrometer. Field desorption (FD) is a method of ion formation used in mass spectrometry (MS) in which a high-potential electric field is applied to an emitter with a sharp surface.

All the bisdiazo compounds were dissolved in THF (HPLC grade) of 10 mg/mL, and about 4 μ L on the direct insertion probe. Ionization was activated with a voltage of -10 kV and a current of 40 mA, the ion source was at OFF mode with a temperature of about 40°C and the temperature of the probe was programmed with an increasing rate of 25.6 mA/min from 0 up to 40 mA. As the probe reaches the current of about 40 mA, its corresponding temperature would be approximately at 600°C. The ion range (*m/z*) monitored by JMS-T2000GC 'AccuTOFTM GC Alpha' system is from 35 to 1600. The original FD chronograms and for mass spectrometric analysis were summarized in Figure S10 and Table S5, respectively.

The possible smaller fragments coming from the decomposition of both compounds are shown in Figure S10c-S10f, which is mainly relied on the m/z data in each region. Those decomposed fragments could be further confirmed by techniques that combing TGA-MS¹³⁻¹⁵ and TGA-IR-MS^{16, 17}.

В	isdiazo-H	Bis	sdiazo-Me	Bis	diazo-NO ₂	Bis	diazo-NH ₂
Region	Time (min)	Region	Time (min)	Region	Time (min)	Region	Time (min)
A1	0.3154-0.6236	D1	0 2208 0 7622	C1	0.2601-0.7432	D1	0.5139-0.6472
A2	0.6319-0.8401		0.2200-0.7023	C2	0.7349-0.9265	20	0 6805 1 1220
A3	0.8568-1.1483	22	0 7056 1 1204	C3	0.9348-1.0431		0.0003-1.1220
A4	1.1483-1.2899	DZ	0.7950-1.1204	C1	1 1190 1 5505	50	0 5130 0 6472
A5	1.2983-1.4648	B3	1.1621-1.5619	- 64	1.1100-1.5595	03	0.5159-0.0472

Table S5. Time in chronograms for mass spectrometric (m/z) analysis





Figure S10. (a, b) FD chronographic traces and (c-f) MS patterns of bisdiazo-R compounds in THF solution upon heating group (colored arrow states the direction of increasing temperature along with longer time), possible structures and monoisotopic m/z of the possible dimer and trimer of (g) bisdiazo-H upon heating (based on the data in regions of A1, A2 and A3 in Figure S10c), that of (h) bisdiazo-NH₂ upon heating before polymerization (based on the data in regions of D1, and D2 in Figure S10f).

Heating rate independence of FD mode measured m/z. Since the bisdiazo compounds are energetic materials, which is well-known for being light and thermal sensitive. Here we also noticed that the FD chronogram is kind of heating up under varied current rate as measurements were carried out, and the sharpness of the band showed in FD chronograms are significantly affected by the corresponding heating rate, therefore the decomposition pattern and releasing of nitrogen could be changed, but not on the detected m/z of the bisdiazo compounds themselves that exhibits the highest intensity signals on the mass spectra of both bisdiazo-H and bisdiazo-NH₂ compounds as demonstrated in Figure S11b and S11d, and the m/z around 28.00 is for releasing a dinitrogen.



Figure S11. FD chronograms and mass spectra of (a, b) bisdiazo-H and (c, d) bisdiazo-NH₂ with (a, c) the current rate of 25.6 mA/min (top-row) and 51.2 mA/min (bottom-row) in the range of 0 to 20 mA.

3 Surface functionalization of PVA thin film by bisdiazo-NH₂

3.1 PVA thin film fabrication

Certain amount of 4.0 g PVA powder (87-89% hydrolysis degree, Mw 146-186 kDa) was added in portions into 100.0 g ultrapure water (resistance 18.2 M Ω ·cm) while being stirred of 450 rpm on a hot plate of 90°C for a couple of hours as the PVA is fully dissolved. Such clear aqueous solution was cooled down to room temperature naturally and followed by sonication for 30 min in a water-bath at room temperature. Then the solution was left to stand and stored at ambient temperature for further use.

3.2 Surface functionalization by bisdiazo-NH₂

Firstly, 2.5 g of 4 wt% PVA aqueous solution was casting into Polytetrafluoroethylene (PTFE) petri-dish (dia. \sim 60 mm), and then followed by being heated in an oven of 60 °C of 24 h, and further ambient drying at room temperature for another 72 hr after being cooled down naturally to room temperature.

Similarly, for surface modification, keep the bisdiazo-NH₂/PVA weight ratio of 20 wt%, and 20 mg bisdiazo-NH₂ in solutions with only dichloromethane (DCM) and DCM plus diethyl ether. Such solution was carefully poured onto the PVA thin film surface in PTFE petri-dish, and under ambient drying at RT for at least for 30 min in dark, then underwent heating in an oven of 120°C for 60 min. Finally cooling down naturally to room temperature for further characterization. As for comparison, the pristine PVA thin film without surface modification was baked in an oven of 120°C for 60 min as well, since further heat treatment might lead to some crystallinity changes in PVA film.

3.3 Characterizations of modified PVA thin films

Morphological analysis of the samples was done by using the Field Emission Scanning Electron (FE-SEM) Microscope Hitachi Regulus 8100 at the accelerating voltage of 2.00 kV. The samples were covered with a 7 nm layer of gold. X-ray photoelectron spectroscopy (XPS) study was carried out using a ThermoScientific K-Alpha Photoelectron Spectrometer equipped with a graphite monochromator and *Al Ka* (hv= 1486.6 eV) radiation with a laser diameter of 400 μ m under vacuum of 2.0×10⁻⁷ mbar. The thin film samples were cut into a square of 5 μ m × 5 μ m and put into the XPS testing chamber. The working voltage and current are 12 kV and 6 mA, respectively. The full range scan is at 100.0 eV with a step of 1.0 eV, while the fine scans are at 50.0 eV with a step of 0.1 eV, and the fine scanning for each sample was repeated and averaged at least five times. The binding energy is calibrated at *C1s* of 284.80 eV. All the data was analyzed by Avantage software.

Thin film surface analysis before and after modification were carried out by using tapping mode Atomic Force Microscopy (AFM, Bruker Dimension Icon) for topography and phase images under ambient conditions, and PeakForce AFM-Quantitative Nanoscale Mechanical (QNM) characterization for mechanical properties simultaneously with topography at the same spatial resolution. This uses a RTESPA-300 probe with spring constant of k = 40 N/m, scanning rate of 1 Hz,

and the PeakForce QNM force range 10-30 nN, while the modulus range is illustrated in the resulting images. A scanning size was $2 \times 2 \mu m^2$ for all the measurements with a digital resolution of 256×256 pixels.

Water contact angle (WCA) was measured (DSA25E, KRÜSS GmbH, Germany) with $1 \mu L$ drop size deionized water at three randomly selected areas. The values of angles were obtained through the associated software.



Figure S12. (a) Photos, (b) SEM image and (c) histogram from SEM images of PVA thin film before and after surface modification by using biadiazo-NH₂ in different solvent system.



Figure S13. XPS fine scanning traces at (a) *C1s*, (b) *O1s* and (c) *N1s* of pristine PVA and bisdiazo-NH₂ compound in different solutions for surface modifications.

Figure S12a shows that the surface color changes before and after surface modification by using bisdiazo- NH_2 and would be subtle in color different as it was dissolved in DCM alone and DCM combined with diethyl ether. There would be insignificant variations from the SEM morphology images as in Figure S12b, but the corresponding histogram from SEM images illustrated in Figure S12c confirmed the subtle color difference from the two surfaces after modification.

While those differences perceived by naked eyes and image processed data like histogram are circumstantial and more likely to be qualitative analysis, and then persuasive quantitative analysis on surface modification like XPS was applied, the results of which

are demonstrated in Figure S13. In Figure S13a, after surface modification by bisdiazo-NH₂ compounds, regardless of solvent system, there are significant changes occurred and carbon are most from the aromatic heavily surface due to the possible polymerization as evidenced by small broad π - π * satellite peak¹⁸. Furthermore, from Figure S13b that noticeable decrease in the O-H peak from O1s in PVA after surface modification and mostly enriched the C-O as in the biscarbene intermediates after polymerization. The most supportive and strong is the rise-up of -NH- in *N1s* scan as illustrated in Figure S13c, which comes only from the bisdiazo-NH₂ compound as compared to that of the bare PVA surface.

4 Density functional theory (DFT) calculations

4.1 Molecular geometry optimized and carbene searching

Before rushing into the molecular dynamic calculations for the possible linkers formed in the dimers as demonstrated in Figure 7 in the main text, the bisdiazo-H and its carbene species should be at its ground state with minimum energy. The DFT calculations were performed using GaussView 6.0¹⁹ and Gaussian 16 program suite²⁰, and the popular hybrid functional B3LYP method (Becke's three-parameter)²¹ with the correlation functional of Lee, Yang, and Parr²² in conjunction with 6-311+G(d, p) basis set²³ with dispersion correction using the schemes of Grimme GD3BJ^{24, 25}was applied for achieving molecular ground state, including the bisdiazo-H, diazocarbene-H and biscarbene, while the carbene species was obtained by using the intrinsic reaction coordinate (IRC) path searching. The sturcure of all the molecular were fully optimized with the absence of negative frequency values in the imaginary one.

The singlet and triplet of diazocarbene-H and biscarbene-H were evaluated at the theory level of UM062X-D3 after being fully optimized at the theory level of B3LYP-D3BJ with the same basis site of 6-311+G(d, p), and the calculated energy states that the triplet one is the ground state with the lowest energy state, which indicates the singlet would be the activated one for the following molecular dynamics calculations.

4.2 Spectrum results

Here, the spectrum results are about the comparison between the calculated IR and UV-Vis and those by experimental ones. The calculated IR are from the frequency calculations as showed Figure S14, while the UV-Vis spectrum in THF as solvent were obtained by using THF as solvents using long-range-corrected functional CAM-B3LYP²⁶ with the basis set of 6-311+G(d, p) and dispersion correction of Grimme type scheme GD3BJ along with the implicit solvation model density (SMD), a widely used continuum solvation model in computational chemistry as illustrated in Figure S15. As can be seen from Figure S14, the theoretical and experimental spectra matched quite well, with identifiable vibration modes at each band of interest for all bisdiazo compounds, as examplified by the IR spectrum of bisdiazo-H in Figure 14a.





Figure S14. Comparison of DFT calculated and experimental IR of bisdiazo-R compounds: (a) R=H, (b) R=Me, (c) R=NO₂, (d) R=NH₂.

Figure S15 details the theoretical and measured UV-Vis spectra of bisdiazo compounds in THF solutions. For bisdiazo-H and bisdiazo-Me, the difference in the major absorption peak between the calculated and measured spectra are small, at 17.89 and 20.28 nm, respectively. For bisdiazo-NO₂ in THF, a measured minor absorption peak at about 246 nm appears as a shoulder-like feature in the calculated UV-Vis curve. While for the UV-Vis spectra of bisdiazo-NH₂ in THF, a minor band was found in experiments that was kind of shadowed in the DFT calculated one. Overall, the differences in the major UV-Vis absorption peak between the TDDFT calculation and measurements are acceptable and accurate enough at the theoretical level of CAM-B3LYP-D3(BJ) along with a SMD solvation model.



Figure S15. Comparison on UV-Vis spectrum of bisdiazo-R compounds in THF obtained by TDDFT calculation and experiment: (a) R=H, (b) R=Me, (c) R=NO₂, (d) R=NH₂,

4.3 Molecular dynamic (MD) calculations for linkers formation in a dimer

For the linker C=C formation from both carbene centered C atoms, a possible dimer structure composed of two identical Diazocarbene-H was explored. While for the other linker C=N-N=C from carbene center C atom and N from a diazo site, another possible dimer composed of a bisdiazo-H and biscarbene-H structures. These two dimers were as illustrated in Figure 8a-8b in the main text. The MD calculations were performed by using a free softwre ORCA 5.0.3²⁷ at the theory level of B97-3c with the default basis set and grids settings through the template showed below, and the results were further analysed by using VMD 1.9.3²⁸. All the calculated input files (XX_MD.inp format), output (XX_MD.out) and trajectory ones (pos#.xyz) were provided as another separate set of attachments. Here, number 1 entitled files for linker C=C and 2 for -C=N-N=C. specifically, in such MD running template, the time step is 1.0 fs for 2000 steps in total at the equilibrium temperature of 298.15K being heated in thermostat model of CSVR, and constraint center atoms were used for maintaining all the atoms are at the mass center of initial system.

(1) file template for MD calculations

e.g., Template_MD.inp

! B97-3c noautostart miniprint nopop

%maxcore 10000

%pal nprocs 12 end

%md

#restart ifexists # Continue MD by reading [basename].mdrestart if it exists. In this case "initvel" should be commented

#minimize # Do minimization prior to MD simulation

timestep 1.0_fs # This stepsize is safe at several hundreds of Kelvin

initvel 298.15_K no_overwrite # Assign velocity according to temperature for atoms whose velocities are not available

thermostat CSVR 298.15_K timecon 30.0_fs # Target temperature and coupling time constant

dump position stride 1 format xyz filename "pos.xyz" # Dump position every "stride" steps

#dump force stride 1 format xyz filename "force.xyz" # Dump force every "stride" steps

#dump velocity stride 1 format xyz filename "vel.xyz" # Dump velocity every "stride" steps

#dump gbw stride 20 filename "wfn" # Dump wavefunction to "wfn[step].gbw" files every "stride" steps

constraint add center 0..115 #Fix center of mass at the initial positio

run 2000 CenterCOM # Number of MD steps. Remove motion of center of mass

end

* xyz 0 1

atomic coordinates of a dimer

*

(2) Coordinates of molecular structures' geometry fully optimized at ground state

bisdiazo-H

C		4 00021100	0 22005000
L	5./10/5/00	-4.99921100	-0.33905000
С	5.01391200	-4.12283800	0.48685200
С	5.27927500	-2.75651300	0.45830400
С	6.25138100	-2.27136600	-0.41522000
С	6.96223500	-3.13425900	-1.24334700
С	6.69314300	-4.50011400	-1.19912000
0	6.60343300	-0.93408000	-0.44783400
С	5.61934600	0.02838300	-0.39739500
С	4.39642500	-0.11598700	-1.05286600
С	3.46778800	0.91496000	-1.00737500
С	3.73373800	2.09879300	-0.30387400
С	4.97477600	2.22770300	0.33329600
С	5.91436800	1.20514000	0.28465400
С	2.72874900	3.17986100	-0.25225300
С	1.28022800	2.99962200	-0.08551300
С	0.36795900	4.00521100	-0.44678000
С	-0.99412800	3.80745100	-0.25661600
С	-1.48100600	2.62008000	0.27920700

С	-0.58690300	1.59885700	0.63749000
С	0.78610500	1.80580800	0.45399000
С	-1.08599000	0.34540500	1.22416600
С	-2.43671700	-0.22037300	1.04669500
С	-3.10916100	-0.09020500	-0.17733000
С	-4.37603200	-0.62906400	-0.36131600
С	-4.99072200	-1.31949900	0.68299100
С	-4.33469900	-1.47472500	1.90089700
С	-3.07179100	-0.92480300	2.07927300
0	-6.21676700	-1.93385900	0.54820600
С	-7.19466800	-1.34552000	-0.23227600
С	-7.48130900	0.01614900	-0.14894400
С	-8.52114700	0.53902800	-0.91263200
С	-9.27477100	-0.28787400	-1.74491500
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С	-7.93978300	-2.18274800	-1.05648800
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N	-0.25693300	-0.33566200	1.96965000
N	3.56114900	5.47449800	-0.40630100
N	0.46941300	-0.92515900	2.62084400
Н	5.50651600	-6.06141800	-0.31013600
Н	4.25864100	-4.50248000	1.16507000
Н	4.74053100	-2.07392500	1.10314900
Н	7.71462300	-2.72523400	-1.90596100
Н	7.24619800	-5.17361100	-1.84334100
Н	4.17884900	-1.02450800	-1.59936500
Н	2.52766400	0.80492200	-1.53295500
Н	5.20328700	3.13012800	0.88876500
Н	6.87093100	1.29844300	0.78314300
Н	0.72101800	4.93350700	-0.87947800
Н	-1.68970400	4.59253300	-0.53019200
Н	-2.54338400	2.48941300	0.43362000
Н	1.48520600	1.03062100	0.73807200
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Н	-4.88001000	-0.52562300	-1.31354700
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Н	-8.74776100	1.59698900	-0.84895400
н	-10.08392900	0.12514200	-2.33481400
н	-9.56434400	-2.29982600	-2.45199000
н	-7.69461200	-3.23675200	-1.09363200

DiazoCarbene-H

С	-5.85540500	4.79830800	-0.35546000
С	-5.65841800	4.42746200	0.97306900
С	-5.77817400	3.09196900	1.35471000
С	-6.09808100	2.14401100	0.39253000
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С	-6.17918200	3.83139800	-1.30714600
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С	-5.33420000	-0.10702300	0.46819900
С	-4.08328500	0.21911900	-0.07222800
С	-3.18417600	-0.79524900	-0.34575300
С	-3.51456200	-2.16266600	-0.14342600
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С	-5.69027100	-1.44347600	0.70581100
С	-2.66291600	-3.25327000	-0.47613400
С	-1.24961800	-3.02540500	-0.53269000
С	-0.49123400	-3.63097700	-1.56295800
С	0.87826000	-3.43044400	-1.63149100

С	1.54696800	-2.71698900	-0.63611700
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C	-0.56060300	-2.27287900	0.44731400
C	1.54177500	-1.41976900	1,49725700
C	2.80995200	-0.68465400	1.35139600
C C	3 13058400	-0.05217100	0 14011600
c c	1 31676900	0.65446100	-0.00863700
c	4.31070900 E 20E27100	0.03440100	1 06105000
	3.20337100	0.74567500	1.00195900
C	4.9012/100	0.13955800	2.27683900
C	3./1619000	-0.5/188400	2.41593100
0	6.36592000	1.48874700	0.99799900
C	7.12942700	1.46660400	-0.15304200
С	7.35148500	0.29385300	-0.87360100
С	8.18322400	0.32958300	-1.98964500
С	8.79570700	1.51929600	-2.38081200
С	8.57201100	2.68143100	-1.64460000
С	7.73659000	2.66080600	-0.53078700
Ν	0.99197800	-1.42355300	2.68225700
Ν	0.51437000	-1.42863500	3.71714200
Н	-5.76103600	5.83696000	-0.64836400
н	-5 41063000	5 17605900	1 71611800
н ц	-5 62087000	2 77019700	2 28066600
	-5.02987900	2.77918700	2.38000000
п 	-0.55895700	1.72913100	-1.05912800
н	-6.33962400	4.11/4/600	-2.33987000
н	-3.82950200	1.25227400	-0.26/12100
н	-2.21643500	-0.54707700	-0.76285100
Н	-5.08174600	-3.48863000	0.49006100
Н	-6.67070400	-1.65353500	1.11427100
н	-1.00761600	-4.23889700	-2.29518000
н	1.44905800	-3.87484800	-2.43900700
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Н	2.43649600	-0.10055800	-0.68901500
Н	4.54812400	1.14218200	-0.94697800
н	5.60291900	0.22382100	3.09717000
н	3.50056000	-1.05582500	3.36158000
н	6.88017200	-0.62958400	-0.56227800
н	8.35864400	-0.58123300	-2.55037000
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Н	7.54794000	3.55268200	0.05353200
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bisediberi			
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С	4.67663000	-3.01353100	0.20074500
С	5.41440100	-2.28044300	-0.72334200
С	5.73486300	-2.79999600	-1.97046800
С	5.30113600	-4.08279800	-2.30141600
0	5.91061900	-1.02596700	-0.38500800
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С	3.70564500	-0.02042700	-0.59580500
С	2.90681600	1.08454500	-0.36206600
C	3.42552200	2,27277900	0.22046600
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C C	5 59983300	1 16744700	0.37739900
C C	2 66825700	2 45701100	0.37735500
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C C	1.24790700	3.35111100	0.00271000
	0.41009400	4.30034400	0.09059300
	-0.90033600	4.50292300	0.25324800
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C	-0./5100400	2.24289900	1.55258500
C	0.64621600	2.30940400	1.36736100
С	-1.29411600	1.20263000	2.37590600
C	-7 10856300	0.57188300	1.95113400
	-2.43830300		
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C C	-2.92034000 -4.06942100	0.47952500 -0.20293700	0.59704300 0.23642800
C C C	-2.92034000 -4.06942100 -4.86737800	0.47952500 -0.20293700 -0.76993900	0.59704300 0.23642800 1.23773800

С	-3.30703800	-0.07475300	2.92522900
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н	3.66887000	-4.87000400	0.57074900
Н	4.44886200	-2.58374900	1.16838100
Н	6.31660300	-2.20154400	-2.66023600
Н	5.54800500	-4.49705300	-3.27171600
Н	3.30316400	-0.90423800	-1.07237500
Н	1.86836700	1.06063200	-0.66655000
Н	5.22039800	3.19915900	0.95160700
Н	6.64678300	1.16011500	0.65341100
Н	0.88048500	5.19511000	-0.40848500
Н	-1.58954700	5.09142100	-0.15417600
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Н	-4.35497900	-0.29630700	-0.80282700
Н	-5.12281800	-1.16508000	3.32935200
н	-2.97197000	-0.04291100	3.95466100
Н	-7.24305000	0.59506500	-0.12274700
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Н	-8.20327400	-1.45124600	-3.78469800
Н	-7.05638800	-3.48116200	-2.93895200
н	-5.99467900	-3.45667700	-0.67925800

(3) Coordinates of molecular structures' geometry fully optimized in THF as solvent at ground state

Bisdiazo-H

С	5.82707200	-4.95491400	-0.24307300
С	5.13680500	-4.06411600	0.57010300
С	5.37021500	-2.69888300	0.48060900
С	6.29751900	-2.23045600	-0.44136800
С	6.99602000	-3.10738700	-1.25757500
С	6.75916700	-4.47124700	-1.15249500
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С	5.62477400	0.05200100	-0.44935400
С	4.40240700	-0.09979300	-1.09191600
С	3.46130700	0.91219800	-1.01637200
С	3.72021400	2.08298900	-0.29968700
С	4.95926700	2.21896900	0.32639600
С	5.91002600	1.21338500	0.25031900
С	2.70992200	3.15821000	-0.22728200
С	1.25813300	2.97774800	-0.07460500
С	0.35872100	3.98170200	-0.44612500
С	-1.00250900	3.78988200	-0.27195400
С	-1.49568700	2.60863100	0.25949100
С	-0.61172200	1.59124200	0.62893600
С	0.75857600	1.79013100	0.45922100
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Ν	0.39284100	-0.88128800	2.67849800
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н	4 41337500	-4 43218400	1 28808300
н Ц	4 83702000	2 00568000	1 11064000
	4.03792000	-2.000000900	1.11904000
	7.71030300	-2.71333900	-1.90304200
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Н	4.18940900	-0.99975500	-1.65481600
Н	2.51762900	0.79263800	-1.53335600
Н	5.18374900	3.11503900	0.89379000
Н	6.86930100	1.31646900	0.74207600
Н	0.71808900	4.90862100	-0.87711700
Н	-1.69232000	4.57582300	-0.55614200
н	-2 56110800	2 48243800	0 39766800
н	1 45088600	1 01035600	0 74865200
 Ц	2 61220000	0.37820500	1 0/133100
	4 92246600	0.57829300	1 2022/100
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Н	-8.73416900	1.60047800	-0.70579200
Н	-10.14828600	0.19860000	-2.18004200
Н	-9.66113400	-2.22208200	-2.40452900
Н	-7.75131600	-3.22204900	-1.16935900
Bisdiazo-M	9		
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C C	5 26624000	3 87573700	0.66454400
0	-5.20024000	3.07373700	0.00434400
	-5.54087400	2.51840500	0.07035000
C	-6.34015500	1.97879500	-0.32262400
С	-6.86929600	2.78348000	-1.31358200
С	-6.59114900	4.14628500	-1.30639800
0	-6.68114200	0.63851700	-0.30917400
С	-5.68935300	-0.30488800	-0.37312500
С	-4.44373800	-0.05961700	-0.93790000
С	-3.50801900	-1.07999000	-0.99826500
C.	-3 78995000	-2 34922800	-0 49241400
	E 0E200700	-2 57632300	0.45241400
C	-3 113 /10//111		
C	-5.05209700	1 56745000	0.11520500
C C	-5.99780100	-1.56745900	0.11538500
C C C	-5.99780100 -2.78198800	-1.56745900 -3.42799700	0.11538500
	-5.99780100 -2.78198800 -1.33913500	-1.56745900 -3.42799700 -3.28531700	0.11538500 -0.55471000 -0.30794400
с с с с	-5.99780100 -2.78198800 -1.33913500 -0.42500200	-1.56745900 -3.42799700 -3.28531700 -4.23348900	0.11538500 -0.55471000 -0.30794400 -0.77806800
C C C C C C C C	-5.05209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800
0000000	-5.05209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200
000000000	-5.05209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600
0 0 0 0 0 0 0 0 0	-5.09780100 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800 -0.86292700	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400
000000000000000	-5.09209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800 -0.86292700 0.97624500	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700 -0.88563700	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400 1.46692900
	-5.09209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800 -0.86292700 0.97624500 2.33543600	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700 -0.88563700 -0.30937900	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400 1.46692900 1.46092900
	-5.09209700 -5.99780100 -2.78198800 -0.42500200 0.92623500 0.92623500 0.49801800 0.49801800 0.97624500 2.33543600 3.06120400	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700 -0.88563700 -0.30937900 -0.24561500	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400 1.46692900 1.44000600 0.25192900
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000000000000000000000000000000000000000	-5.05209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800 -0.86292700 0.97624500 2.33543600 3.06120400 4.33376200 4.89346300	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700 -0.88563700 -0.30937900 -0.24561500 0.30587800 0.81827500	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400 1.46692900 1.44000600 0.25192900 0.21366900 1.37704800
000000000000000000000000000000000000000	-5.09209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800 -0.86292700 0.97624500 2.33543600 3.06120400 4.33376200 4.89346300 4.18011000	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700 -0.88563700 -0.30937900 -0.24561500 0.30587800 0.81827500 0.77662200	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400 1.46692900 1.44000600 0.25192900 0.21366900 1.37704800 2.56967700
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2	-5.09209700 -5.99780100 -2.78198800 -1.33913500 -0.42500200 0.92623500 1.39636000 0.49801800 -0.86292700 0.97624500 2.33543600 3.06120400 4.33376200 4.89346300 4.89346300 4.18011000 2.91857800 6.13203100 6.95703800 7.69384800 8.55366900 8.69469400 7.07569300 3.21817200	-1.56745900 -3.42799700 -3.28531700 -4.23348900 -4.08233000 -2.99611400 -2.03444300 -2.19358700 -0.30937900 -0.24561500 0.30587800 0.30587800 0.24561500 0.30587800 0.24561500 0.21210700 1.39852700 1.32959900 0.18044400 0.14314700 1.24152200 2.43342700 2.43342700	0.11538500 -0.55471000 -0.30794400 -0.77806800 -0.51150800 0.21007200 0.68054600 0.41699400 1.46692900 1.44000600 0.25192900 0.21366900 1.37704800 2.56967700 2.59838000 1.43304000 0.32249700 0.08053000 -1.0603400 -1.58491800 -0.50112000 0.82282000
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ĉ	6 87203000	2 48656100	1 12721000
ĉ	6 71005000	2.40000100	1 1112131900
	-0.71025200	3.63353900	-1.41131600
0	-6.64483300	0.64232600	0.38851800
С	-5.66845800	-0.26312300	0.07883700
С	-4.46558000	0.07414700	-0.52984500
С	-3.53681800	-0.91888700	-0.80547800
С	-3.77871200	-2.24931500	-0.46948000
С	-4.99377100	-2.56618800	0.14317600
С	-5.93375600	-1.58802700	0.40908200
Ċ	-2 78338200	-3 29980300	-0 77246300
Č	-1 32836800	-3 10081200	-0 58783700
ĉ	0.45242200	4 07234600	1 24240000
0	-0.43242200	-4.07234000	-1.24249900
C	0.91274000	-3.96730500	-1.03220200
C	1.43470300	-3.00141700	-0.18590000
С	0.57524600	-2.11622500	0.47067900
С	-0.80043500	-2.22865500	0.26206100
С	1.11225200	-1.10138800	1.38979100
С	2.49745300	-0.58736600	1.41528100
С	3.18472000	-0.32453100	0.23206400
С	4 48077400	0 17083100	0 24645600
Ċ	5 10322500	0 42664800	1 46216500
ĉ	4 42003000	0.1812/000	2 65384000
ĉ	4.42303000	0.10124000	2.00004000
0	3.143/0900		2.02004200
0	0.3/454600	0.91008000	1.5/85/000
C	7.09350500	1.1963/000	0.42429900
С	7 92171800	0.22976100	-0.11997800
С			
С	8.67844100	0.52297500	-1.24367000
<u> </u>	8.67844100 8.61673300	0.52297500 1.78818000	-1.24367000 -1.83486400
C	8.67844100 8.61673300 7.77800500	0.52297500 1.78818000 2.75161900	-1.24367000 -1.83486400 -1.26684900
c	8.67844100 8.61673300 7.77800500 7.02206700	0.52297500 1.78818000 2.75161900 2.45733600	-1.24367000 -1.83486400 -1.26684900 -0.14309100
C N	8.67844100 8.61673300 7.77800500 7.02206700 -3.24436000	0.52297500 1.78818000 2.75161900 2.45733600 -4.42451100	-1.24367000 -1.83486400 -1.26684900 -0.14309100 -1.22400900
C C N N	8.67844100 8.61673300 7.77800500 7.02206700 -3.24436000 0.29718700	0.52297500 1.78818000 2.75161900 2.45733600 -4.42451100 -0.61508100	-1.24367000 -1.83486400 -1.26684900 -0.14309100 -1.22400900 2.27367000
	8.67844100 8.61673300 7.77800500 7.02206700 -3.24436000 0.29718700 -3.64388800	0.52297500 1.78818000 2.75161900 2.45733600 -4.42451100 -0.61508100 -5 41104300	-1.24367000 -1.83486400 -1.26684900 -0.14309100 -1.22400900 2.27367000 -1.61530700

N	-0.41787500	-0.19548200	3.04736300
Н	-5.22515600	4.81565200	1.47101500
Н	-5.51807100	2.40863200	1.96989100
Н	-7.33678200	1.82397700	-1.84786600
Н	-7.05090800	4.22915900	-2.36171800
Н	-4.25206800	1.09962100	-0.79849200
Н	-2.61055100	-0.64597200	-1.29565000
Н	-5.20670600	-3.59211400	0.42233900
Н	-6.87448100	-1.83538300	0.88535800
Н	-0.83369300	-4.82803000	-1.91892900
Н	1.58426500	-4.65144500	-1.53767600
Н	2.50294400	-2.94368000	-0.02731800
Н	-1.47408400	-1.55271800	0.77208700
Н	2.70403800	-0.50195400	-0.72187500
Н	4.99245400	0.36515200	-0.68623900
Н	4.92774800	0.38231500	3.59398500
Н	2.63658100	-0.52886100	3.56355300
Н	7.97334400	-0.75113800	0.33755100
Н	9.32797300	-0.23372600	-1.66973300
Н	7.72255000	3.73925600	-1.71105300
Н	6.37461800	3.20714000	0.29604700
N	-5.90018900	6.03237300	-0.78937400
N	9.33552600	2.06669000	-2.99382900
Н	10.15285200	1.49182200	-3.14357200
Н	9.52369200	3.04539600	-3.16045400
Н	-6.51619700	6.41804200	-1.49124500
Н	-5.79924000	6.64640700	0.00662100

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Appendix. MATLAB code and data files

• The code attached below are the plots shown in Figure 4d and 4f in main text.

clc; close all;

```
filename = 'C:\Users\xiaosong.liu\Documents\MATLAB\efsNH2.xlsx';
% data file named efs.xlsx for all compounds polymerized at 120degC, while
```

```
% another one named efsNH2.xlsx for Bisdiazo-NH2 compound polymerized at 66-
% 100-120degC
data = readtable(filename);
parameter_names = data.Var1;
p1 = data.p1;
p2 = data.p2;
p3 = data.p3;
p4 = data.p4;
x = 1:0.2:8;
y1 = zeros(length(p1), length(x));
y2 = zeros(length(p3), length(x));
for i = 1:length(p1)
    y1(i, :) = p1(i) * exp(-x / p2(i)); % decomposited exponential part
    y2(i, :) = p3(i) + p4(i) * x;
                                         % decomposited linear part
end
figure;
subplot 121;
hold on;
for i = 1:length(p1)
    plot(x, y1(i, :), 'DisplayName', parameter_names{i});
end
title('y_1=p_1 exp(-x/p_2)');
xlabel('x=ln(t/min)');
% ylabel('y_1=p_1 exp(-x/p_2)');
legend;
grid on;
subplot 122;
hold on;
for i = 1:length(p3)
    plot(x, y2(i, :), 'DisplayName', parameter_names{i});
end
title('y 2=P 3+p 4 x');
xlabel('x=ln(t/min)');
% ylabel('y2');
legend;
grid on;
```

• Parameter data files of efs.xlsx and efsNH2.xlsx

Hereby, the fitted parameters shown in the bellowing tables are obtained from the kinetic described by using Eq.(S11). The parameters shown in bellowing tables of efs.xlsx and efsNH2.xlsx were explored for plots shown in Figure 5d and Figure 5f, respectively, in the main text.

Table S5. Parameters for file efs.xlsx

|--|

Н	5.26638	0.66579	-0.50351	0.01305
Me	2.21872	1.03312	-0.51098	0.01813
NO ₂	0.75187	1.35369	-0.27281	0.02402
NH ₂	5.57463	1.1402	-1.6458	0.16084
-				

Table S6. Parameters for file efsNH2.xlsx

	р1	p2	р3	р4
66°C	14.8413	25.79015	-14.3218	0.0.37661
100°C	14.7673	6.5077	-12.3914	0.92635
120°C	5.57463	1.1402	-1.6458	0.16084